

# Quantifying system disturbance and recovery from historical mining-derived metal contamination at Brotherswater, northwest England

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## **Keywords**

Lake sediments; Metal contamination; Pb mining; Sediment flux; Disturbance; System  
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## Abstract

Metal ore extraction in historical times has left a legacy of severe contamination in aquatic ecosystems around the world. In the UK, there are ongoing nationwide surveys of present-day pollution discharged from abandoned mines but few assessments of the magnitude of contamination and impacts that arose during historical metal mining have been made. We report one of the first multi-centennial records of lead (Pb), zinc (Zn) and copper (Cu) fluxes into a lake (Brotherswater, northwest England) from point-sources in its catchment (Hartsop Hall Mine and Hogget Gill processing plant) and calculate basin-scale inventories of those metals. The pre-mining baseline for metal contamination has been established using sediment cores spanning the past 1,500 years and contemporary material obtained through sediment trapping. These data enabled the impact of 250 years of local, small-scale mining (1696 – 1942) to be quantified and an assessment of the trajectory towards system recovery to be made. The geochemical stratigraphy displayed in twelve sediment cores show strong correspondence to the documented history of metal mining and processing in the catchment. The initial onset in 1696 was detected, peak Pb concentrations ( $>10,000 \mu\text{g g}^{-1}$ ) and flux ( $39.4 \text{ g m}^{-2} \text{ y}^{-1}$ ) corresponded to the most intensive mining episode (1863-1871) and 20<sup>th</sup> century technological enhancements were reflected as a more muted sedimentary imprint. After careful evaluation, we used these markers to augment a Bayesian age-depth model of the independent geochronology obtained using radioisotope dating ( $^{14}\text{C}$ ,  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$  and  $^{241}\text{Am}$ ). Total inventories of Pb, Zn and Cu for the lake basin during the period of active mining were 15,415 kg, 5,897 kg and 363 kg, respectively. The post-mining trajectories for Pb and Zn project a return to pre-mining levels within 54-128 years for Pb and 75-187 years for Zn, although future remobilisation of metal-enriched catchment soils and floodplain sediments could perturb this recovery. We present a transferable paleolimnological approach

that highlights flux-based assessments are vital to accurately establish the baseline, impact and trajectory of mining-derived contamination for a lake catchment.

## Introduction

Historical mining and metal ore processing has resulted in potentially toxic concentrations of metals building up in waterways and lakes (Blais et al. 2015). Metal-enriched effluent may discharge directly from a mine, spoil heap or smelter into aquatic systems (Audry et al. 2004; Mayes et al. 2013; Boyle et al. 2015a), while the emission and subsequent atmospheric deposition of metal particulates can also be a source of contamination across much wider scales (Renberg et al. 1994; Brännvall et al. 2001; Rippey and Douglas 2004). Point-source contamination from mining activities can significantly exceed atmospheric supply (Farmer et al. 1997; Yang and Rose 2005; Thevenon et al. 2011). As a result, the European Union Water Framework Directive (WFD) (2000/60/EC) and subsequent Mining Waste (2006/21/EC) Directive mandate the remediation of contaminated runoff from abandoned mining sites as one pre-requisite to aquatic systems achieving ‘Good’ ecological status (Johnston et al. 2008). Site-specific reference conditions, or the background metal concentrations expected in an undisturbed (pre-human impact) lake system, provide a basis for evaluating progress towards this goal (Bindler et al. 2011). In the UK, thresholds for permissible levels of metals in river and lake waters have been set (UKTAG 2010). Draft guidelines for the concentrations present in sediments have been put forward by the UK Environment Agency (Hudson-Edwards et al. 2008) but formal sediment quality criteria used by governmental agencies elsewhere in the world (Burton 2002; MacDonald et al. 2000) have not yet been adapted. A national-scale assessment of contemporary contaminated discharge from abandoned mines has recently been conducted (Mayes et al. 2009; 2010), but few assessments have been made of historical metal fluxes during peak ore extraction in the 19<sup>th</sup> century. Sediment records preserved in lakes offer unique opportunities to reconstruct the magnitude of mining-derived contamination (Farmer et al. 1997; Couillard et al. 2007;

Parviainen et al. 2012; Schindler and Kamber 2013) and establish reference baselines for metals (Bindler et al. 2011) on a catchment-specific basis.

The Lake District in northwest England has a mining heritage that extends back to the Bronze Age (Adams 1988), with peak ore production between the 1800s and 1940s. This legacy is reflected in the sediments of a number of regional lakes, with evidence detected for contamination from local mines (Hamilton-Taylor 1983; Anderton et al. 1998; Grayson and Plater 2008), coal-fired steamboat and railway emissions (Miller et al. 2014) and atmospherically derived deposition (Rippey and Douglas 2004; Yang and Rose 2005). These studies have rarely, however, calculated long-term, basin-scale fluxes and inventories of mining-derived metals. At Ennerdale and Wastwater (western Lake District), 20<sup>th</sup> century metal mass accumulation rates were linked to atmospheric emissions from regional coal and lead consumption (Hamilton-Taylor 1983). Longer-term estimates were compiled by Farmer et al. (1997) for Loch Tay, central Scotland, where lead extraction occurred at the Tyndrum mine 25 km upstream, and Yang et al. (2002a) for Lochnagar, a small tarn in northeast Scotland, where atmospheric input dominates the anthropogenic inventory of Pb and Hg. Thus, we do not have a good grasp of point-source historical metal fluxes even for small mines located in close proximity to a lake.

Here we tested an approach using multiple sediment cores to quantify both the spatial and temporal patterns of catchment-to-lake, mining-derived metal flux (Pb, Zn, Cu) at Brotherswater, eastern Lake District, United Kingdom. Our aim was to establish the pre-mining baseline concentrations in the lake and quantify the contamination history by calculating fluxes and inventories of accumulated metals during phases of mine operation in the catchment. By sampling the recent sedimentation using cores and sediment traps we also sought to assess the trajectory and progress towards system recovery since the cessation of ore extraction in 1942.

## Study site

Brotherswater is a small ( $0.18 \text{ km}^2$ ), upland (158 m above sea level) lake with a comparatively large catchment ( $13.01 \text{ km}^2$ ) in the eastern Lake District (Fig. 1). The catchment displays a steep relief (maximum elevation 792 m) and forest cover has almost entirely been replaced over the last millennium by open hill grazing and some improved pasture. A substantial mantle of glacial sediment covered by shallow, podzolic-brown earth soils susceptible to erosion provide ample sediment supply. In the lake, a single inflow from the southwest has formed a steep-fronted gravel (2- to 10-cm diameter) Gilbert-style delta and the bathymetry is dominated by a flat (maximum 18 m) central basin. This configuration minimises the possibility of wind-induced re-suspension affecting the sediment record as the basin is deeper than the high-risk zone for small lakes with restricted fetch calculated by Dearing (1997). The lake waters are classified as close to the oligo/mesotrophic boundary, display summer (June-August) thermal stratification and their pH ranges annually between 6.8 and 7.4 (Maberly et al. 2011).

### *Mining at Hartsop Hall*

The English Lake District experienced small-scale Bronze Age and Roman Era metal extraction, more extensive Medieval operations (1200 – 1400) and an intensifying industrial phase from 1550 (Adams 1988) until falling metal prices, depleted reserves and competition with global markets led to the decline of the UK industry around 1940 (Byrne et al. 2010). Hartsop Hall Mine lies 600 m to the southwest of Brotherswater on the east-facing flank of Hartsop-above-How hill ( $54^{\circ}29'55''\text{N}$ ,  $2^{\circ}56'9.74''\text{W}$ ; Figs. 1c, 2). Miners exploited an

argentiferous galena (PbS) vein, which dissects the Lincomb Tarns and Esk Pike Sandstones of the Borrowdale Volcanic Series of Ordovician age (circa 450 Mya) along a NE-SW bearing (Stanley and Vaughan 1982). This vein relates to a regional ‘galena-sphalerite’ highly saline (marine), low temperature (110-130°C) mineralization phase during the early-Carboniferous (Stanley and Vaughan 1982). Ores are set in quartz and predominantly composed of galena, moderate amounts of sphalerite (ZnS) and baryte (BaSO<sub>4</sub>) and minor quantities of chalcopyrite (CuFeS<sub>2</sub>) and silver (Ag) (Tyler 1992). Wulfenite (PbMoO<sub>4</sub>) and fluorite (CaF<sub>2</sub>) are present but below extractable quantities (Adams 1988; Tyler 1992).

Tyler’s (1992) collated history of Hartsop Hall Mine provides lease and operation dates, but not precise ore production figures. The first short-term lease dates from 17<sup>th</sup> April 1696, concurrent with operations at a 17<sup>th</sup> century water-mill and smelter at Hogget Gill, 500 m southwest of the mine (54°29'33” N, 2°56'42” W; Fig. 1c). Galena extraction volumes of 2,450 kg and 6,230 kg were estimated from contractual documents for two short-lived, early-19<sup>th</sup> century ventures at Hartsop Hall (1802-04 and 1830-32, respectively) that failed due to inadequate financing. Water-powered milling (1863-71) allowed Hartsop Hall to operate at peak capacity (24,000 kg yr<sup>-1</sup>) and coincides with anecdotal evidence for discoloration of Kirkstone Beck, fish kills and acute livestock poisoning (Tyler 1992). Later efforts (1931-1942) were mechanically enhanced, typified by more efficient Pb recovery from harvested ores, and processing shifted to the larger Greenside Mine, approximately 20 km north of Brotherswater (Tyler 1992; Grayson and Plater 2008). Archived records also reference minor extraction of Cu that occurred at Caiston Glen Copper Mine (54°28'59N, 2°56'4”W; Fig. 1c) around 1870-1880 (Tyler 1992).

Today, abandoned mining infrastructure and exposed waste materials are visible across the hillslopes at Hartsop Hall Mine (Fig. 2). The mine entrance and spoil heaps are elevated ~100 m directly above Dovedale and Kirkstone Becks. Overland flow incising through spoil piles

downslope to the streams is visible after moderate rainfall and remnants of a functioning leat (Figs. 1, 2) are another potential connection between the mining waste and river system.

## **Materials and methods**

### **Core collection**

Twelve sediment cores between 24.5- and 339-cm in length were extracted from ten profundal locations in March 2011 and October 2012 (Fig. 1d; Table 1), comprising overlapping hand-percussive Russian-style drives (chamber length 100- or 150-cm, diameter 7.5-cm) and short gravity cores (8-cm diameter) to capture the sediment-water interface intact. Coring sites were selected to radiate from delta-proximal to more distal locations and characterize the fluvially-derived sediment dispersal within the lake.

### **Sediment trapping**

Near-monthly lake sediment trapping was undertaken between 08/2012 and 12/2013 for the purpose of comparing contemporary metal fluxes with the uppermost depositional record. Traps collected material at three depths (100, 75 and 25% of total water depth) near the delta (75 m from the inflow, core site BW11-2) and a mid-lake site (225 m from the inflow, core site BW12-9). The cylindrical PVC traps with removable sampling cups (Schillereff 2015a) have a 1:6.8 aspect ratio (11-cm diameter: 75-cm length) to minimize re-suspension and ensure representative capture of sediment flux through the water column (Bloesch and Burns 1980).



## Geochemical analyses

Major element and trace metal concentrations were determined on each core using one of three Energy Dispersive (ED) X-ray fluorescence (XRF) instruments (Table 1). The long cores BW11-1, BW11-4, BW11-5 and BW12-9 were  $\mu$ XRF-scanned (Olympus Delta ED-XRF) on a wet sediment basis at 0.5-cm intervals using a Geotek MSCL-XZ core scanner and wet sediment samples from core BW11-3 were measured manually on a Thermo-Niton ED-XRF. Wet sediment element concentrations were converted to dry-weight equivalent (Boyle et al. 2015b) using a training set of dried samples (BW12-9A) measured on a Bruker S2 Ranger ED-XRF analyser equipped with a Pd X-ray tube and Peltier-cooled silicon drift detector. Dry mass concentrations were corrected for organic matter content (Boyle 2000). Subsamples were taken at 0.5-cm intervals from all other cores except BW11-7 (4-cm) and BW11-8 (1-cm) (Table 1). All core and sediment trap samples that were measured on the S2 Ranger ED-XRF had previously been freeze-dried and their moisture contents and dry bulk densities (assuming average grain density =  $2.65 \text{ g cm}^{-3}$ ) calculated. Each XRF analyser undergoes a daily standardization procedure using certified reference materials (Boyle et al. 2015b).

## Geochronology

Delta-proximal (BW11-2) and distal (BW12-9) cores were dated radiometrically ( $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$ ,  $^{137}\text{Cs}$ ,  $^{241}\text{Am}$ ) by direct gamma assay using Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detectors at the Liverpool Environmental Radioactivity Laboratory (Appleby et al. 1986). Sub-samples were measured at 1.5- to 4-cm (BW11-2) and 1- to 2-cm (BW12-9) intervals to pinpoint the convergence of fallout  $^{210}\text{Pb}$  with *in situ*  $^{226}\text{Ra}$  activity and detect peaks in artificial radionuclide ( $^{137}\text{Cs}$ ,  $^{241}\text{Am}$ ) concentrations that

potentially reflect known releases of these radionuclides to the atmosphere. The longer BW11-2 sequence was dated using thirteen  $^{14}\text{C}$  measurements that targeted hand-picked terrestrial plant macrofossils (Table 2). All  $^{14}\text{C}$  samples were pre-treated using a standard Acid-Alkali-Acid wash to remove dissolved humic acids, converted to carbon dioxide by combustion in quartz tubes and graphitised by iron-zinc reduction at the SUERC Laboratory (East Kilbride, Scotland).

## Results

### Spatial patterns of sediment and metals accumulation

Pb profiles in the lake sediments show persistent low concentrations ( $<100 \mu\text{g g}^{-1}$ ) at depth and a pronounced, repeatable stratigraphy in the upper sections of the 12 cores (Fig. 3). This striking pattern varies in depth across the lake, with less sediment accumulating with greater distance from the delta. Concentrations increase from the low baseline through a series of peaks (reaching  $\sim 2,000 \mu\text{g g}^{-1}$ ) to a dominant spike (Fig. 3; Table 3). Notwithstanding slight overestimation in the conversion of  $\mu\text{XRF}$  scan data to equivalent dry mass concentrations at maximum Pb values (Boyle et al. 2015b), the Pb peak exceeds  $10,000 \mu\text{g g}^{-1}$  in delta-proximal cores and exceeds  $4,000 \mu\text{g g}^{-1}$  more widely across the basin. Peak Pb occurs at 82 cm depth in BW11-3, contrasting with its appearance at depths of 17-20 cm beyond 350 m from the inflow. Above this feature Pb concentrations initially fall sharply and then decline slowly towards the surface but maintain concentrations higher than the pre-mining baseline ( $>500 \mu\text{g g}^{-1}$ ). One additional minor peak at 56 cm depth in BW11-3 can be traced across all cores.

## Geochronology

BW11-2 showed clear 1963 (atmospheric weapons testing) and 1986 (Chernobyl) peaks in  $^{137}\text{Cs}$  and  $^{241}\text{Am}$  at 21.5 and 9.5 cm depth, respectively (Fig. 4a). The punctuated decline of unsupported  $^{210}\text{Pb}$  activity and variations in sediment accumulation rate (SAR) before the 1940s diminish the reliability of the  $^{210}\text{Pb}$  ages calculated for this period. BW12-9 produced a more coherent  $^{210}\text{Pb}$  chronology based on the constant rate of supply (CRS) model (Appleby and Oldfield 1978), which is corroborated by the presence of  $^{137}\text{Cs}$  and  $^{241}\text{Am}$  peaks at 10.25 and 5 cm depth (Fig. 4b). The pre-1940  $^{210}\text{Pb}$  curve was transferred reliably to BW11-2 by correlating multiple geochemical profiles.

A preliminary age-depth model was generated for BW11-2 using the Bayesian routine ‘Bacon’ (Blaauw and Andrés Christen 2011) that integrated the sediment surface (2011), the radiocarbon ages,  $^{137}\text{Cs}$  and  $^{241}\text{Am}$  peaks and the  $^{210}\text{Pb}$  curve transferred from BW12-9. This modelling approach partitioned the core into 5-cm-thick sections and estimated the accumulation rate for each segment using a Markov Chain Monte Carlo (MCMC) approach, constrained by prior information on accumulation rate (a gamma distribution with mean 5-year  $\text{cm}^{-1}$  and shape 2) and its variability (memory, a beta distribution with mean 0.5 and shape 20).  $^{14}\text{C}$  ages were calibrated using the IntCal13 curve (Reimer et al. 2013) and modelled within ‘Bacon’ using a Student-t distribution, which better takes into account scatter in the  $^{14}\text{C}$  measurements and allows for statistical outliers in the model (Christen and Pérez 2009). This model revealed a largely coherent integration of the radiometric dating techniques ( $^{14}\text{C}$ ,  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$  and  $^{241}\text{Am}$ ) although five radiocarbon ages diverged from the MCMC best-fit output. Pairs at 41-50.5 cm and 127-151 cm plot as anomalously old and a single age at 225 cm appears too young. Two reliable stratigraphical markers were then identified in the XRF-derived Pb profile of BW11-2 and assigned ages of 1696 and 1863.

These were assigned narrower error distributions (i.e., parameters  $t.a$  and  $t.b$  were set to 33 and 34, respectively, in Bacon) and incorporated into a revised Bayesian age-depth model (Fig. 5).

## Sediment and metal fluxes

Mass accumulation rates (MAR) and fluxes for metals provide a more meaningful assessment of the degree of contamination because the approach incorporates the effects of changing sediment supply. Bulk density values were determined for three cores: BW11-3, BW11-2 and BW12-9. Pb, Zn and Cu fluxes were calculated for BW11-2 and 12-9, but only Pb data were measured on core 11-3. These three cores were selected as they lie along a delta-proximal to distal transect and encompass the basin-wide variation in accumulation rate (Fig. 3). The cores show down-lake gradients of both declining mass accumulation rate and metal flux (Fig. 6), although this reduction is not linear with distance from the inflow. This matches the pattern present more widely in the depths of peak Pb across the lake (Fig. 3).

Pb fluxes for BW11-3, 11-2 and 12-9 show low, stable levels ( $<0.1 \text{ g m}^{-2} \text{ y}^{-1}$ ; Fig. 6) below an initial increase that exceeded 1, 0.3 and  $0.2 \text{ g m}^{-2} \text{ y}^{-1}$ , respectively (zone 1, Fig. 6). The short-lived but prominent feature at 82 cm (BW11-3), 58 cm (BW11-2) and 25 cm (BW12-9) exhibits the maximum fluxes for Pb of 39.4, 36.0 and  $1.56 \text{ g m}^{-2} \text{ y}^{-1}$ , respectively (zone 2, Fig. 6). Some minor peaks occur towards the surface, with zone 3 showing the largest Pb increase not wholly driven by greater sediment flux. The Zn and Cu fluxes mirror the initial onset of elevated Pb (zone 1, Fig. 6:  $0.6$  and  $0.08 \text{ g m}^{-2} \text{ y}^{-1}$ , respectively, in BW11-2) and the notable 1860s spike (zone 3:  $1.6$  and  $0.18 \text{ g m}^{-2} \text{ y}^{-1}$ ), but the patterns differ markedly above this feature. They fluctuate and remain high (maximum  $2.7$  and  $0.22 \text{ g m}^{-2} \text{ y}^{-1}$ ) during the 20<sup>th</sup> century, appearing more tightly associated to variations in MAR throughout

the record. Sediment traps deployed at Brotherswater between 08/2012-12/2013 recorded monthly Pb concentrations in the range 400-800  $\mu\text{g g}^{-1}$  and MAR-corrected Pb fluxes of 0.1-0.9  $\text{g m}^{-2} \text{yr}^{-1}$  (Fig. 7). Encouragingly, these values are similar to the measurements of the most recently-accumulated core material.

## Discussion

### Metal geochronological markers

The concentrations of Pb, Zn and Cu in the Brotherswater sediments vastly exceed published values for atmospheric fallout recorded in European lake sediments ( $<600 \mu\text{g g}^{-1}$  Pb and Zn: Farmer et al. 1997; Renberg et al. 2001; Rippey and Douglas 2004; Yang and Rose 2005). Maximum concentrations ( $>10,000 \mu\text{g g}^{-1}$  Pb: Fig. 3; Table 3;  $>1,000 \mu\text{g g}^{-1}$  Zn) are similar to other regional and global lakes that received contamination directly from a mine, such as Ullswater, England ( $30,000 \mu\text{g g}^{-1}$  Pb: Grayson and Plater 2008) and Lac Caron, Canada ( $1,500 \mu\text{g g}^{-1}$  Zn: Couillard et al. 2007). These levels indicate metal loading at Brotherswater is almost certainly derived from local sources in the catchment. Well-defined features in lake sediment geochemical profiles linked to pollution histories have been successfully employed as dating points elsewhere (Renberg et al. 2001; Hammarlund et al. 2007). Similar assessment of potential geochronological markers at Brotherswater was undertaken incrementally to negate circular reasoning when developing the chronology. A first-pass Bayesian model using only the radionuclide dating confirmed temporal associations between sedimentary Pb profiles and the documented mining history. These markers were subsequently incorporated into the Bayesian age-depth model (Fig. 5).

Low metal concentrations and fluxes characterize the basal sediments of all cores (Figs. 3, 6), and were classed as the pre-mining baseline. The first rise of metal input most

likely reflects the initiation of mining operations at Hartsop Hall and ore processing (water-milling and smelting) at Hogget Gill in 1696 (Tyler 1992), and forms a chronological marker (124 cm) that can be reliably inserted into the BW11-2 age-depth model. Financial pressures restricted operations during the early-19<sup>th</sup> century at Hartsop Hall to short intervals: 1802-1804 and 1830-1832 (Tyler 1992). The imprint of these minor phases is observed in the BW11-2 Pb profile (onsets at 108.5, 99.5 and 89 cm), but their use as markers in the age-depth model is equivocal and was avoided. Mine records indicate galena extraction peaked during the 1860s at 24,000 kg yr<sup>-1</sup>, at least 12 times greater than early-19<sup>th</sup> century phases. Moreover, anecdotal evidence suggests water-borne contamination during 1860s mining was particularly acute, triggering fish kills and livestock poisoning (Tyler 1992). Making a temporal link between maximum Pb levels (58 cm depth in BW11-2) and major 1860s ore extraction would be justified without independent chronological support. That said, the BW12-9 <sup>210</sup>Pb curve constrains peak Pb concentrations at 25 cm depth to slightly before 1880, firmly associating this major stratigraphical feature with intensive mining 1863-1871 (Fig. 4b). This represents a second chronological marker suitable for the age-depth model. Lastly, the BW12-9 radionuclide data ascribes the elevated Pb levels at 15-17.5 cm depth to the 1930s, the last period of ore extraction at Hartsop Hall (Fig. 4).

#### The refined Bayesian age-depth model

Five <sup>14</sup>C ages appear anomalous in the best-fit model for core BW11-2 and warrant examination, conducted here in reverse chronological order. The two most recent <sup>14</sup>C ages (SUERC-48896 and 48897) produced near-identical probability distributions and plot old relative to the model, probably reflecting sediment remobilization during late-19<sup>th</sup> century alterations of the inflow. The <sup>14</sup>C calibration curves for the last 250 years produce wide

probability distributions and multiple equally-likely age solutions for individual samples as a result of fluctuations in atmospheric  $^{14}\text{C}$  due to fossil fuel combustion (Hua 2009). These issues appear to impact the  $^{14}\text{C}$  measurements at 61 cm (SUERC-48898) and 81 cm (SUERC-48899) (Fig. 5). Incorporating the reliable Pb age markers (first mining in 1696 at 124 cm and onset of peak mining in 1863 at 58 cm) into the Bayesian model (red diamonds) with narrowed probability distributions resolves some of this temporal uncertainty and produces good convergence of  $^{14}\text{C}$  ages at 61 and 81 cm (Fig. 5). The five  $^{14}\text{C}$  ages between 125 cm and 225 cm require careful consideration on the basis of their non-sequential stratigraphy. The  $^{14}\text{C}$  ages at 173 cm (SUERC-48906) and 198 cm (SUERC-48907) show the best fit to the Bayesian model, leaving two anomalously old measurements (SUERC-48903 and SUERC-48904) and one more difficult to explain that is too young (SUERC-48908). Reversals in series of  $^{14}\text{C}$  measurements of equivalent age have been reported for other lakes in the region (Pennington 1991; Edwards and Whittington 1991; Chiverrell 2006; Langdon et al. 2004) and reflect the incorporation of ‘old carbon’ during periods of enhanced erosion of catchment soils (Edwards and Whittington 2001; Chiverrell et al. 2007). The 1696 Pb marker strongly supports the model presented in Fig. 5. The most likely explanation of the young outlier is contamination of some kind during the laboratory preparation or processing stages. The repeatable geochemical profiles of Pb and other elements (Ti, K, Zr; not shown) (Schillereff 2015b) enabled the BW11-2 master chronology to be accurately and precisely transferred to other cores.

### Controls and conditioning of metal fluxes

Sediment accumulation rates (SARs) since the 1860s have been four times more rapid near the delta and sediment focusing (Engstrom and Rose 2013) to the central basin appears to

have a minor depositional effect in Brotherswater. Differing sediment accumulation rates between sites and across individual lake basins (Fig. 3) makes fluxes a preferable comparative tool but such data are rarely reported, and none from mining-affected catchments. Hamilton-Taylor (1983) estimated Pb, Zn and Cu fluxes from two large lakes in the western Lake District that experienced atmospheric deposition of metals during 19<sup>th</sup> century industrialisation but lacked a catchment source. These were five orders of magnitude smaller than the Brotherswater maximum: 0.2, 0.05 and 0.005 g m<sup>-2</sup> yr<sup>-1</sup>, respectively. Maximum Pb flux to Lochnagar, a small Scottish loch known to receive primarily atmospheric input, was similar - 0.021 g m<sup>-2</sup> yr<sup>-1</sup> (Yang et al. 2002a) - and mean atmospheric Pb flux across the UK has rarely exceeded 0.03 g m<sup>-2</sup> yr<sup>-1</sup> since 1850 (Rippey and Douglas 2004). These comparisons reinforce the notion that mining activities in the Brotherswater catchment led to the striking metal concentrations recorded in the lake sediments.

The Brotherswater sedimentary reconstructions reveal a clear imprint of the timescale of ore production and local processing, but also conditioning of the record by technical innovations at the extraction and processing stages (Fig. 6). The initial rise of Pb is interpreted to result from the first documented activity in 1696. Despite the short-term lease and low extraction volumes, early smelting techniques were inefficient. This left substantial waste ore in surface spoil heaps and accelerated the delivery of weathered sulphides and particulates to the watercourses, as seen at Loch Tay (Farmer et al. 1997). Metal particulate emissions are known to have been high during early processing techniques (Ek and Renberg 2001) so a notable airborne contribution is possible. Company records indicate peak ore production occurred during the 1860s and 1870s. While the contribution from the concurrent increase in MAR must also be considered, Pb concentrations exceeding 10,000 µg g<sup>-1</sup> require a local source; we propose that the unusually high Pb concentrations and flux (1.56 - 39.4 g m<sup>-2</sup> y<sup>-1</sup>) reflect direct discharge of contaminated effluent into Kirkstone Beck from a new



crushing mill and open-cast excavations at the Level 3 shaft in Hartsop Hall Mine (Fig. 2; Tyler 1992). This mining activity probably increased sediment delivery into the river, which in turn exacerbated the metal flux. Pb concentrations during 1930s mining are lower than preceding mining episodes. Company documents indicate processing was moved to Greenside Mine and more efficient and mechanised ore extraction techniques were employed, capable of harvesting a greater proportion of the ore from the host rock and leaving less surface waste (Tyler 1992). Pb continued to fluctuate after the cessation of mining in 1942: subsequent peaks probably relate to the remobilisation of mining waste during flood events in the 1960s (Schillereff et al. 2014; Schillereff et al. 2016). Any atmospheric signal from leaded petrol in automobiles during 1950-70 (von Storch et al. 2003) was likely masked by the particulate flux from the catchment.

Previous research at Brotherswater found no evidence for post-depositional remobilisation in the sediment column (Rae and Parker 1993) or bottom-water redox conditioning driven by ferromanganese enrichment (no correlation is observed between Fe and Pb ( $p > 0.6$ ) and Mn and Pb ( $p > 0.4$ )). These are processes that have altered pollution records at other lakes (Boyle et al. 1998). We suggest that post-depositional diffusion is negligible at Brotherswater as the advective solid-phase fluxes of these metals are so great (Boyle 2001; Couillard et al. 2004).

As trace metals were transported into the lake bound to suspended particulate matter in the sediment plume, the process of sediment diffusion across Brotherswater exerts a strong control over the spatial distribution of Pb and this is consistent with theory on the rates of particle settling for metals in profundal sediments (Boyle et al. 1998). This pattern differs from larger lakes in the Lake District contaminated by mining waste. At Ullswater, Pb concentrations decline moderately with distance from inflows receiving waste from Greenside Mine, but SAR varies little through the lake (Grayson and Plater 2008). Likewise,

smaller water-bodies upstream of Windermere act as pollutant sinks, reducing the quantity of mining-related heavy metals reaching Windermere and allowing Pb sourced from coal and latterly diesel-powered steamboats to dominate the down-core profiles (Miller et al. 2014). These results show first-order lakes like Brotherswater are the primary sink for mining-derived material, thus they are likely to experience more persistent negative environmental impacts, whilst offering the best localities for reconstructing histories of past mining.

The Zn and Cu flux profiles suggest different drivers are active: Zn and Cu accumulation rates display a stronger association with variations in sediment flux than Pb (Fig. 6). The onset of mining (1696) triggered slightly higher Zn and Cu fluxes and a more substantial response during the 1860s. Maximum Cu flux during Phase 2 (Fig. 6) probably incorporates a direct contribution from operations at Caiston Glen Copper Mine, active around 1860 – 1870. The Zn and Cu flux after peak mining are strikingly different from that of Pb, however. The significant amplitude of fluctuations in Zn and Cu follows the 20<sup>th</sup> century MAR, but this does not fully explain the persistent elevated concentrations contrasted with Pb. One plausible explanation stems from galena deposits being the primary target at Hartsop Hall, leaving greater quantities of sphalerite and copper ores as unworked, exposed waste, leading to a proportionally greater dissolution and efflux of Zn and Cu (Byrne et al. 2010). The humid temperate climate and flood-dominated hydrological regime generate prevalent oxidizing conditions in the fluvial system (Zoumis et al. 2001), which may have accentuated Zn and Cu concentrations in the lake sediments owing to the greater solubility of their oxidized products (Nuttall and Younger 2002).

Pb, Zn and Cu inventories

Whole-basin inventories of Pb, Zn and Cu accumulation in the Brotherswater sediments were calculated for time intervals of interest from the BW11-3, 11-2 and 12-9 flux information (Table 4), following the method of Yang et al. (2002b). The uneven sediment thickness across the basin was accounted for through a kriging procedure that determined the area of accumulating sediments represented by each core: BW11-3 = 0.016 km<sup>2</sup>, BW11-2 = 0.022 km<sup>2</sup> and BW12-9 = 0.14 km<sup>2</sup>, the latter assumed to represent the central and eastern basins. In total, 15,415 kg of Pb is estimated to have accumulated in the Brotherswater sediments through the period of active ore extraction (1696 – 1942), averaging ~63 kg per year (compared to ~3 kg per year pre-mining) and peaking during the 1860s at 1,141 kg per year. This is equivalent to ~5% of total Pb extracted per year at Hartsop Hall during this period (Tyler 1992). The scale of locally-sourced Pb contamination at Brotherswater is emphasized by comparison to Lochnagar, a small (0.1 km<sup>2</sup>) Scottish upland loch where 150.3 kg of Pb has been stored since 1860 (Yang et al. 2002a), sourced via atmospheric deposition. Zn and Cu inventories reveal that ore extraction contributed a greater loading, but substantially less was delivered to Brotherswater compared to Pb (Table 4). During the measured pre-mining sedimentation (1500 – 1696) the basin-wide Zn inventory exceeded that of Pb by 360%, whereas total Pb loading was 161% greater than Zn after mining commenced. The andesite that dominates the Borrowdale Volcanic Series is heavily enriched in Zn with respect to Pb (McConnell et al. 2002) and a geochemical survey of catchment soils (Hardy 2013) reveals similar Zn enrichment in the B horizon. This indicates the greater pre-mining Zn flux most likely reflects the proportionally-greater input of weathered bedrock and subsoils.

Maberly et al. (2011) found Pb levels below their instrumental limits of detection while monitoring the water chemistry of Brotherswater, suggesting that Pb delivered in particulate form makes a significant contribution to the contemporary loading. Quantifying the legacy of metals delivered from abandoned mining sites to fluvial systems should thus encompass

assessment of these particulate fluxes. Sedimentary records potentially offer a mechanism for monitoring and reconstructing this particulate component over long temporal scales.

## Post-mining trajectory

The UK has not currently set mandatory standards for metal concentrations in sediments, though draft guidelines exist for concentrations in river sediments and surface waters (Hudson-Edwards et al. 2008; UKTAG 2010). The mean threshold calculated from published consensus values elsewhere in the world (MacDonald et al. 2000; Burton 2002) indicate harmful effects are possible if Pb concentrations exceed  $47 \mu\text{g g}^{-1}$ , likely above  $155 \mu\text{g g}^{-1}$  and potentially severe above  $236 \mu\text{g g}^{-1}$ . Sediment deposition at Brotherswater has exceeded the midrange threshold since the onset of small-scale operations at Hartsop Hall in 1696 and substantially surpassed extreme levels since mining intensified in the 19<sup>th</sup> century. In terms of Zn, concentrations have consistently exceeded the global mean extreme threshold ( $649 \mu\text{g g}^{-1}$ ) since peak mining in the 1860s. The story for Cu is less severe, remaining at levels where harmful effects are possible and only briefly exceeding the ‘extreme effect’ guidelines of some countries in the 1860s. Our sediment trapping at Brotherswater shows excessive levels of Pb persist today (Fig. 7). Combining the trap results with the longer sediment record offers insight into the post-mining adjustment or recovery of the system. Mean Pb concentrations from 1942 (year of mine closure) until 2011 for cores BW11-3, 11-2 and 12-9 were 1,188, 806 and  $425 \mu\text{g g}^{-1}$ , respectively. Mean Zn concentrations for the latter two cores over the same period were 647 and  $700 \mu\text{g g}^{-1}$ . Variable river flow may explain the fluctuating post-1942 metal profiles, but all profiles have followed a negative trajectory (declining metal concentrations) since the cessation of mining. Fitting a least squares linear model and using a sediment threshold of  $47 \mu\text{g g}^{-1}$  for Pb suggests the system will return to safe, background

levels (equivalent to pre-mining) in 54-128 years. For Zn, the pristine baseline ( $<146 \mu\text{g g}^{-1}$ ) could be achieved in 75-187 years. Performing the same calculations for the flux data generates equivalent values and shows these declines are not a function of sediment MAR and dilution of the geochemical data.

Measurements of catchment soils and alluvial and deltaic sediment stores (Young et al. 1992; Hardy 2013) down-system of the mine and smelter revealed Pb concentrations typically around  $100 \mu\text{g g}^{-1}$  and  $1,000 \mu\text{g g}^{-1}$  at a few sites closest to the mine. This shows that mining waste has been incorporated and is potentially available for erosion and transfer through the catchment. Thus, despite the on-going decline in metal concentrations in the lake, it is possible that remobilisation of metals in long-term storage may delay concentrations reaching the stable pre-mining baseline for a longer period (Dennis et al. 2009). These findings have notable implications for the development of remediation strategies. Some heavily polluted lakes near Wawa, Canada (Greenaway et al. 2012) and Lake Malären, Sweden (Renberg et al. 2001) have displayed a marked recovery after progressive emission reductions or closures of industry, but intensive remediation efforts have had more limited impact elsewhere: Falun, Sweden (Ek and Renberg 2001) and Goldenville, Nova Scotia, Canada (Wong et al. 1999). While lakes can operate as ‘safe’ sinks for metals, it is a well-known risk that re-suspended material can lead to more acute toxicity in aquatic ecosystems (Fetters et al. 2016). Remediation work at Hartsop Hall Mine is not a current priority for the UK Environment Agency (Johnston et al. 2008); our estimate that metal concentrations may remain above pre-mining levels for up to another 190 years means this decision could merit re-consideration.

## **Conclusions**

Lake sediment records such as that preserved at Brotherswater demonstrate geochemical data can provide a quantitative, historical perspective on anthropogenic metal contamination from local mining activity. The ‘pristine’ pre-mining baseline was characterised as consistent concentrations of Pb below  $100 \mu\text{g g}^{-1}$ . A strong and responsive association between accumulated metal concentrations and the intensity of ore extraction at Hartsop Hall Mine was detected, rising initially in 1696, fluctuating through the early 19<sup>th</sup> century and peaking ( $\text{Pb} > 10,000 \mu\text{g g}^{-1}$ ) during the 1860s, the period of greatest ore extraction. Improved techniques adopted in the 20<sup>th</sup> century reduced contaminant release and muted the metal imprint in the sediment sequence. Careful assessment revealed that these features in the metal profiles offered precise geochronological markers that improved the fit of a Bayesian age-depth model constructed from radioisotope dating. After the cessation of mining in 1942, the recent sediment record suggests a return to pre-mining baseline conditions (i.e., a recovery of the system) will occur in 54-187 years, if the present trajectory is maintained. Our approach emphasises that the calculation of basin-scale fluxes and inventories using lake sediments in catchments affected by mining can contribute to the identification, quantification and environmental monitoring of metal contamination. Recently-accumulated lakebed sediments and estimates of present-day metal fluxes (i.e., through sediment trapping) represent largely-untapped tools for assessing the trajectory of catchments towards system recovery.

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## Tables

**Table 1** Details of the twelve sediment cores

Core ID	Sampling date	Core length (cm)	Measurement resolution (cm)	XRF technique
BW11-1	March 2011	60	0.5	Geotek Olympus (wet)
BW11-2	March 2011	339	0.5	S2 Ranger (dry)
BW11-3	March 2011	264.5	0.5	Thermo-Niton (wet)
BW11-4	March 2011	72	0.5	Geotek Olympus (wet)
BW11-5s	March 2011	19.5	0.5	S2 Ranger (dry)
BW11-5	March 2011	152	0.5	Geotek Olympus (wet)
BW11-6s	March 2011	26	0.5	S2 Ranger (dry)
BW12-7	October 2012	142	4	S2 Ranger (dry)
BW12-8	October 2012	132	1	S2 Ranger (dry)
BW12-9s	October 2012	24.5	0.5	S2 Ranger (dry)
BW12-9	October 2012	134	0.5	Geotek Olympus (wet)
BW12-10s	October 2012	25	0.5	S2 Ranger (dry)

**Table 2** Radiocarbon dates used for the construction of the Brotherswater age-depth model. Dates were integrated into a Bacon Bayesian model (Blaauw and Andrés Christen 2011) and calibrated using the IntCal13 calibration curve (Reimer et al. 2013)

Publication Code	Sample Identifier	$^{14}\text{C}$ Enrichment (% Modern $\pm 1\sigma$ )	Conventional Radiocarbon Age (years BP $\pm 1\sigma$ )	Carbon content (% by wt.)	$\delta^{13}\text{C}_{\text{VPDB}}$ ‰ $\pm 0.1$
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SUERC-48896	BW11-2 RC1 41-42	95.42 ± 0.53	377 ± 45	46.3	-27.765
SUERC-48897	BW11-2 RC2 49-50.5	95.48 ± 0.53	371 ± 45	43.7	-27.879
SUERC-48898	BW11-2 RC3 61-62.5	97.55 ± 0.54	199 ± 45	48.7	-28.3
SUERC-48899	BW11-2 RC4 81-81.5	97.02 ± 0.54	243 ± 45	44.2	-26.098
SUERC-48903	BW11-2 RC6 127-128.5	89.84 ± 0.50	860 ± 45	40.6	-27.351
SUERC-48904	BW11-2 RC7 150-151	90.38 ± 0.51	812 ± 45	41.2	-29.119
SUERC-48906	BW11-2 RC9 172-174	92.26 ± 0.52	647 ± 45	50.5	-28.752
SUERC-48907	BW11-2 RC10 197-198.5	90.85 ± 0.52	771 ± 46	46.1	-27.862
SUERC-48908	BW11-2 RC11 224-224.5	92.99 ± 0.54	584 ± 47	54.9	-30.719
SUERC-48909	BW11-2 RC12 269-270	87.03 ± 0.49	1116 ± 45	53.7	-28.506
SUERC-48910	BW11-2 RC13 321.5-323.5	84.08 ± 0.47	1393 ± 45	50.4	-28.959
SUERC-48913	BW11-2 RC14 335.5-336	82.66 ± 0.46	1530 ± 45	52.5	-28.384
SUERC-35378	BW11-2 (3) 258		930 ± 30		-25.0

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**Table 3** Maximum and mean lead (Pb) concentrations for selected intervals with historical mining significance in core BW11-2.

Depth (cm)	Historical Period (Years)	Maximum Pb Concentration ( $\mu\text{g g}^{-1}$ )	Mean Pb Concentration ( $\mu\text{g g}^{-1}$ )
0-33.5	Post-mining (1942-2011)	1,372	807
33.5-42.5	Mechanised mining (1931-1942)	2,152	1,163
49.5-62	Peak mining (1863-1871)	12,367	3,489
77-109	Early-19 <sup>th</sup> century mining (1802-1832)	875	450
109-124	Response to first mining (1696-1802)	248	159
124-339	Pre-mining (500-1696)	90	62

**Table 4** Lead, zinc and copper inventories for Brotherswater. Values refer to total metal loading within each interval.

Time interval (Year)	Historical Period	Pb Inventory (kg)	Zn Inventory (kg)	Cu Inventory (kg)
1500-1696	Baseline period	392	878	58
1696-1802	First Mining	1,584	939	61
1802-1863	Early-19 <sup>th</sup> century Mining	1,281	1,418	83
1863-1871	Peak Mining	9,126	1,825	131
1871-1931	Mine inactivity	1,758	961	58
1931-1942	Mechanised Mining	1,666	754	30
1942-2011	Post-mining	5,524	3,927	243
1696-1942	Mining total	15,415	5,897	363

## Figure captions

**Fig. 1** A) Location of the English Lake District within the UK. B) Topography and waterbodies of the English Lake District. The Brotherswater catchment is shaded black and

lakes mentioned in the text are labelled. C) Catchment Digital Elevation Model highlighting the location of ore extraction and processing sites in the Brotherswater catchment. D) Bathymetric map (2-m contours) of Brotherswater showing the ten coring locations. Note both a short and a long core were extracted at sites BW11-5 and BW12-9, labeled with an 's' in the text and subsequent Figs. A colour version is available online.

**Fig. 2** The view west across the floodplain of Brotherswater highlighting the location of Hartsop Hall mining infrastructure, shaft levels, exposed waste heaps and their proximity to the river. The levels were sunk incrementally, with the first ore extracted from level 1 and shafts 3 and 4 dug during peak mining in the 1860s and 1870s. A colour version is available online.

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**Fig. 5** Age-depth model for core BW11-2 that integrates thirteen radiocarbon ages (blue symbols),  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  radionuclide dating for recent sediments (green) and Pb mining markers in red. The pathway followed to establish the Pb geochronological markers is elaborated upon in the text. A colour version is available online.

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**Fig. 7** Measured Pb concentrations and calculated Pb flux through the period of sediment trapping. Site A is adjacent to core site BW11-2 and Site B was situated at core site BW12-9.

## Tables

**Table 1** Details of the twelve sediment cores

Core ID	Sampling date	Core length (cm)	Measurement resolution (cm)	XRF technique
BW11-1	March 2011	60	0.5	Geotek Olympus (wet)
BW11-2	March 2011	339	0.5	S2 Ranger (dry)
BW11-3	March 2011	264.5	0.5	Thermo-Niton (wet)
BW11-4	March 2011	72	0.5	Geotek Olympus (wet)
BW11-5s	March 2011	19.5	0.5	S2 Ranger (dry)
BW11-5	March 2011	152	0.5	Geotek Olympus (wet)
BW11-6s	March 2011	26	0.5	S2 Ranger (dry)



BW12-7	October 2012	142	4	S2 Ranger (dry)
BW12-8	October 2012	132	1	S2 Ranger (dry)
BW12-9s	October 2012	24.5	0.5	S2 Ranger (dry)
BW12-9	October 2012	134	0.5	Geotek Olympus (wet)
BW12-10s	October 2012	25	0.5	S2 Ranger (dry)

**Table 2** Radiocarbon dates used for the construction of the Brotherswater age-depth model. Dates were integrated into a Bacon Bayesian model (Blaauw and Andrés Christen 2011) and calibrated using the IntCal13 calibration curve (Reimer et al. 2013)

Publication Code	Sample Identifier	$^{14}\text{C}$ Enrichment (% Modern $\pm 1\sigma$ )	Conventional Radiocarbon Age (years BP $\pm 1\sigma$ )	Carbon content (% by wt.)	$\delta^{13}\text{C}_{\text{VPDB}}$ ‰ $\pm 0.1$
SUERC-48896	BW11-2 RC1 41-42	$95.42 \pm 0.53$	$377 \pm 45$	46.3	-27.765
SUERC-48897	BW11-2 RC2 49-50.5	$95.48 \pm 0.53$	$371 \pm 45$	43.7	-27.879
SUERC-48898	BW11-2 RC3 61-62.5	$97.55 \pm 0.54$	$199 \pm 45$	48.7	-28.3
SUERC-48899	BW11-2 RC4 81-81.5	$97.02 \pm 0.54$	$243 \pm 45$	44.2	-26.098
SUERC-48903	BW11-2 RC6 127-128.5	$89.84 \pm 0.50$	$860 \pm 45$	40.6	-27.351
SUERC-48904	BW11-2 RC7 150-151	$90.38 \pm 0.51$	$812 \pm 45$	41.2	-29.119
SUERC-48906	BW11-2 RC9 172-174	$92.26 \pm 0.52$	$647 \pm 45$	50.5	-28.752
SUERC-48907	BW11-2 RC10 197-198.5	$90.85 \pm 0.52$	$771 \pm 46$	46.1	-27.862

SUERC-48908	BW11-2 RC11 224-224.5	$92.99 \pm 0.54$	$584 \pm 47$	54.9	-30.719
SUERC-48909	BW11-2 RC12 269-270	$87.03 \pm 0.49$	$1116 \pm 45$	53.7	-28.506
SUERC-48910	BW11-2 RC13 321.5-323.5	$84.08 \pm 0.47$	$1393 \pm 45$	50.4	-28.959
SUERC-48913	BW11-2 RC14 335.5-336	$82.66 \pm 0.46$	$1530 \pm 45$	52.5	-28.384
SUERC-35378	BW11-2 (3) 258		$930 \pm 30$		-25.0

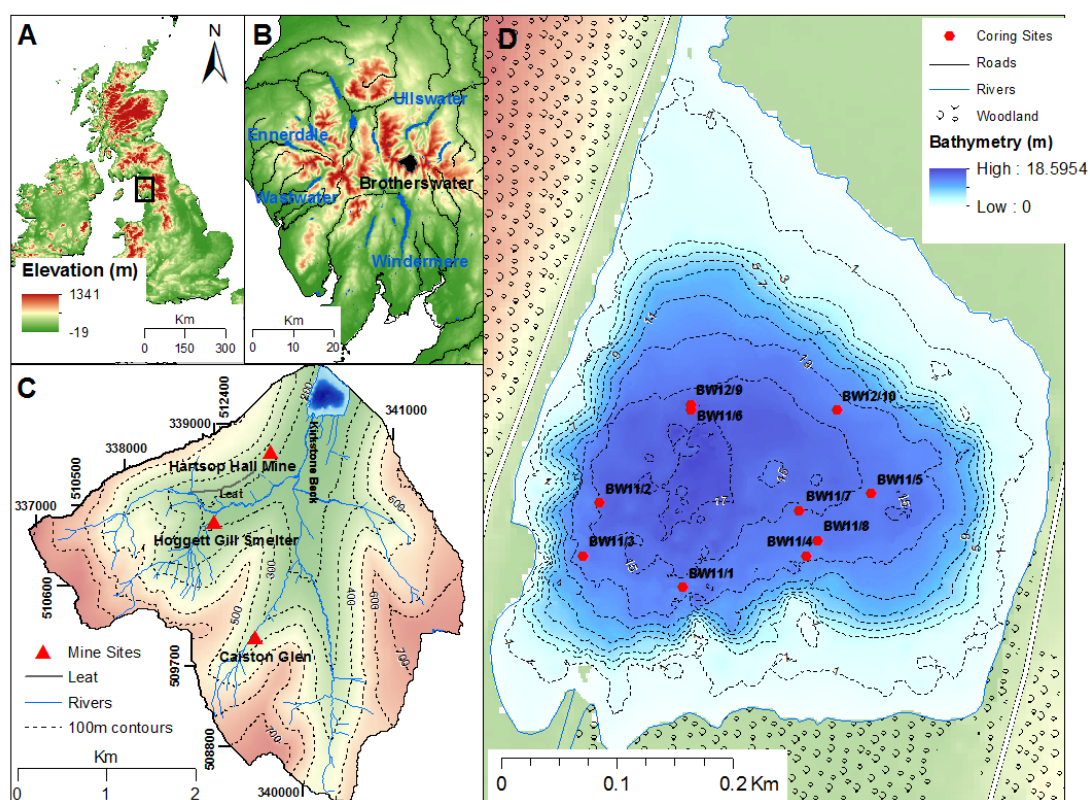
**Table 3** Maximum and mean lead (Pb) concentrations for selected intervals with historical mining significance in core BW11-2.

Depth (cm)	Historical Period (Years)	Maximum Pb Concentration ( $\mu\text{g g}^{-1}$ )	Mean Pb Concentration ( $\mu\text{g g}^{-1}$ )
0-33.5	Post-mining (1942-2011)	1, 372	807
33.5-42.5	Mechanised mining (1931-1942)	2, 152	1, 163
49.5-62	Peak mining (1863-1871)	12, 367	3, 489
77-109	Early-19 <sup>th</sup> century mining (1802-1832)	875	450
109-124	Response to first mining (1696-1802)	248	159
124-339	Pre-mining (500-1696)	90	62

**Table 4** Lead, zinc and copper inventories for Brotherswater. Values refer to total metal loading within each interval.

Time interval (Year)	Historical Period	Pb Inventory (kg)	Zn Inventory (kg)	Cu Inventory (kg)
1500-1696	Baseline period	392	878	58
1696-1802	First Mining	1584	939	61
1802-1863	Early-19 <sup>th</sup> century Mining	1281	1418	83
1863-1871	Peak Mining	9126	1825	131
1871-1931	Mine inactivity	1758	961	58
1931-1942	Mechanised Mining	1666	754	30
1942-2011	Post-mining	5524	3927	243
1696-1942	Mining total	15415	5897	363

## Figures

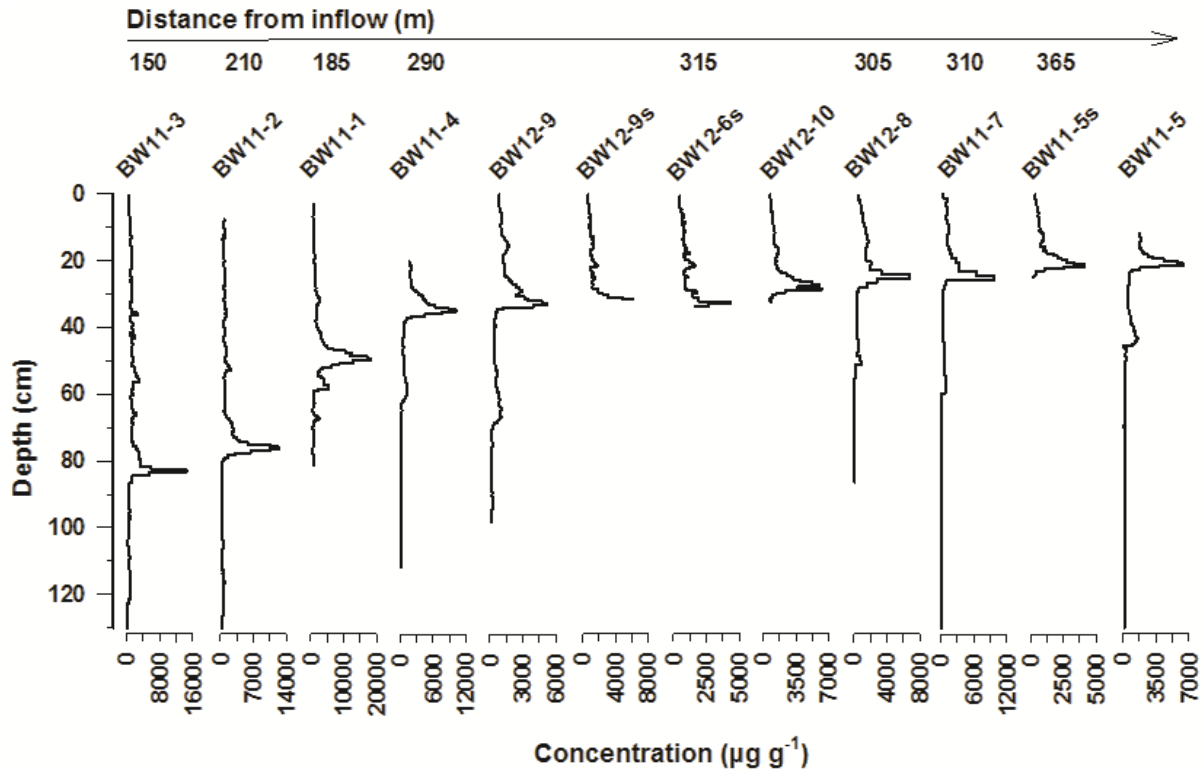


**Fig. 2** A) Location of the English Lake District within the UK. B) Topography and waterbodies of the English Lake District. The Brotherswater catchment is shaded black and lakes mentioned in the text are labelled. C) Catchment Digital Elevation Model highlighting the location of ore extraction and processing sites in the Brotherswater catchment. D)

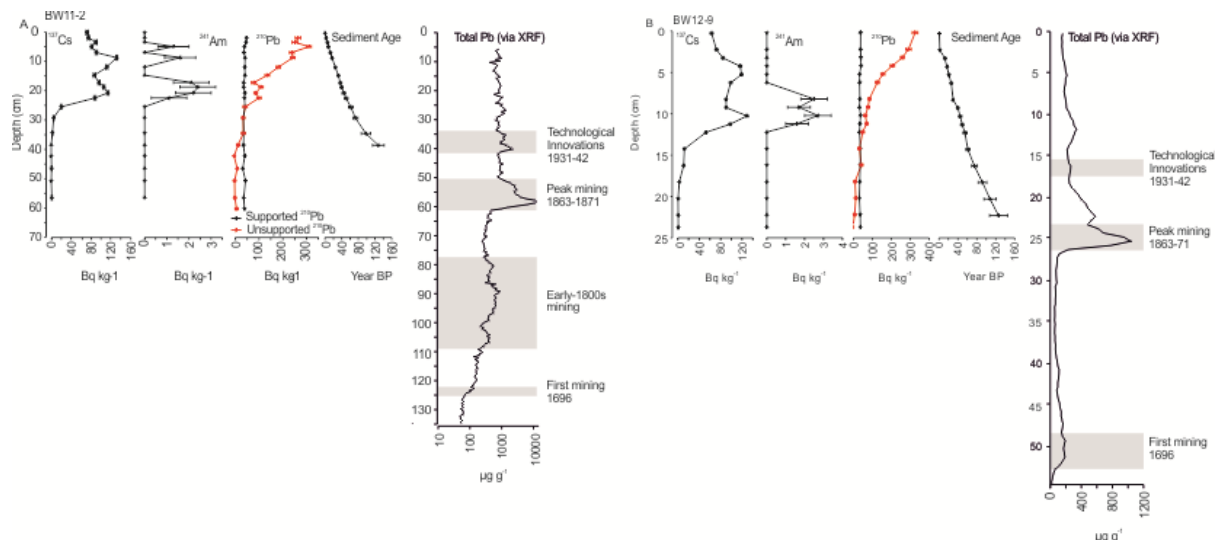
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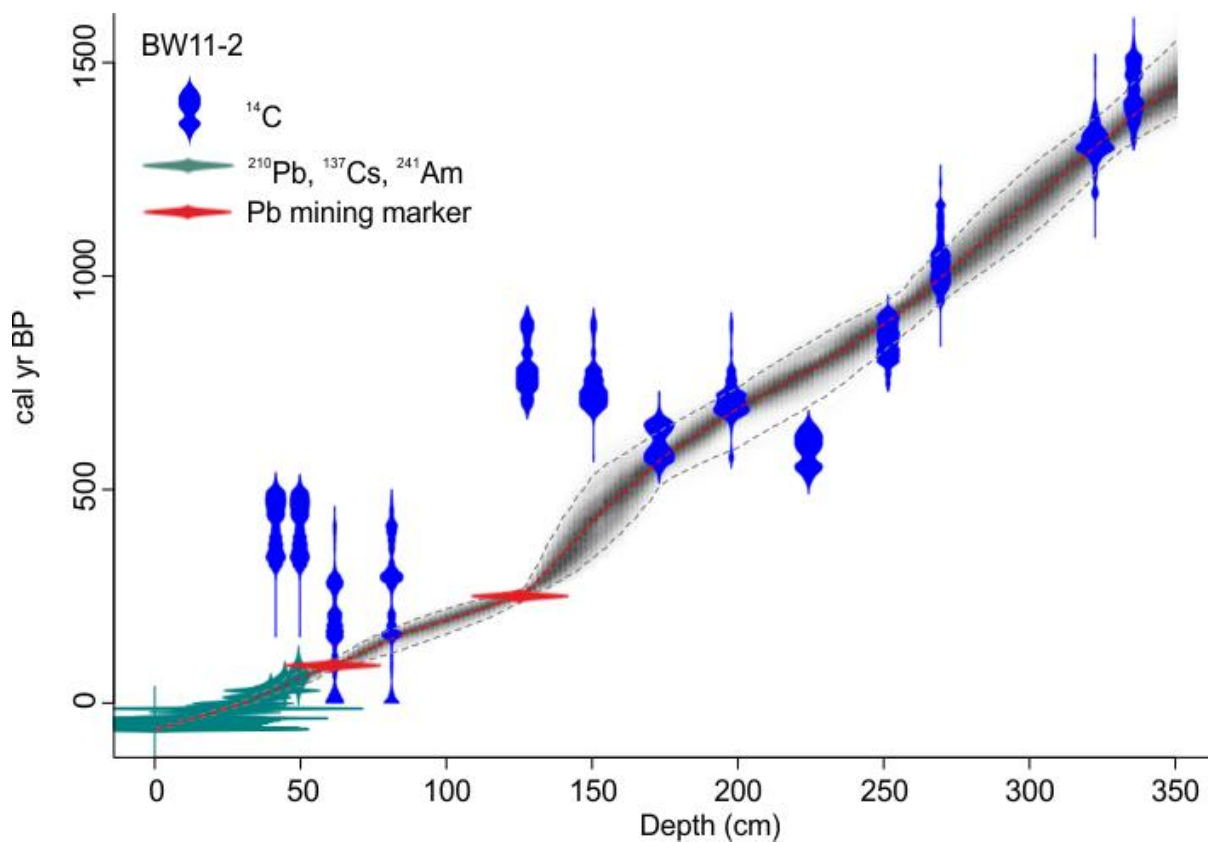
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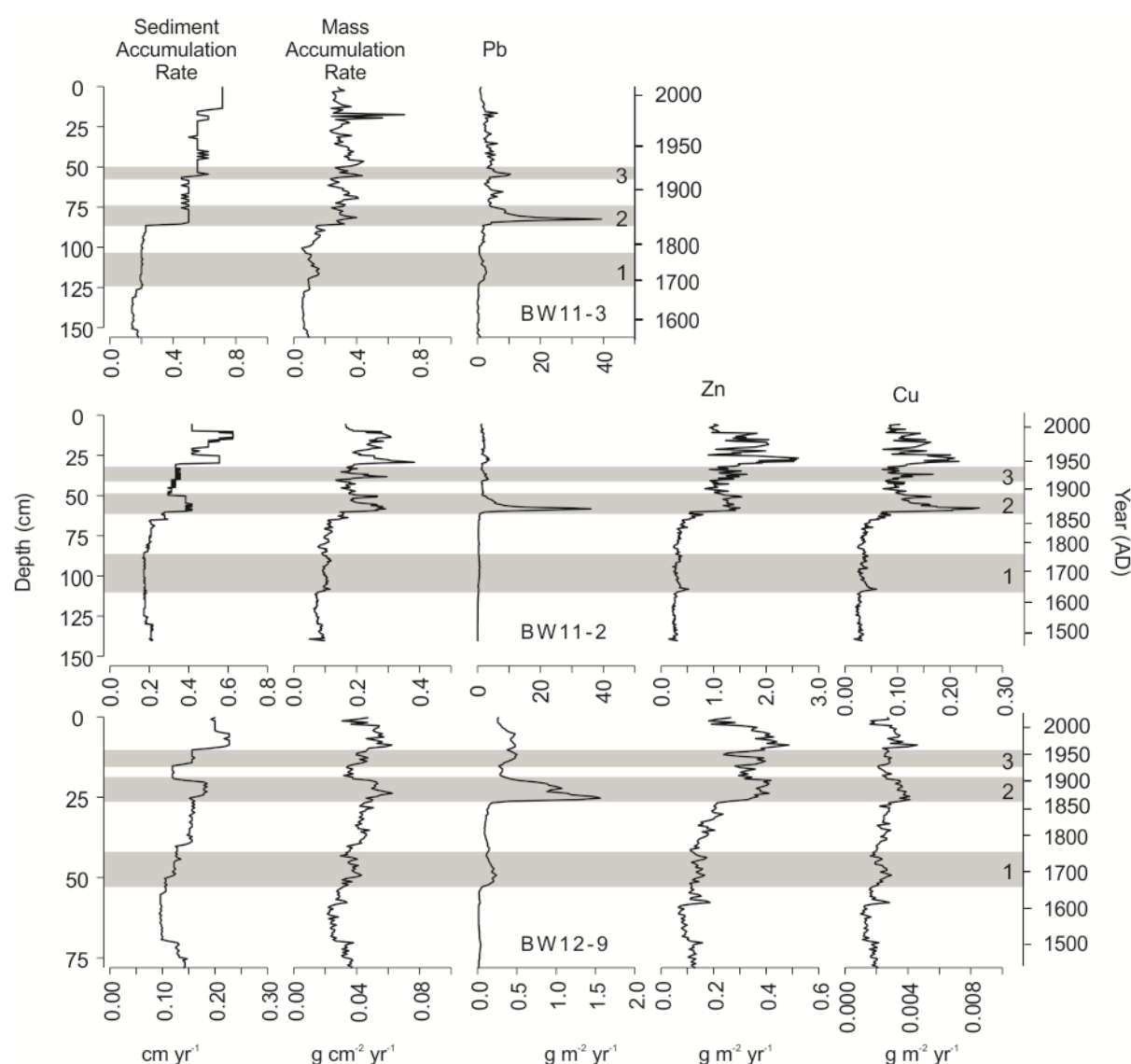


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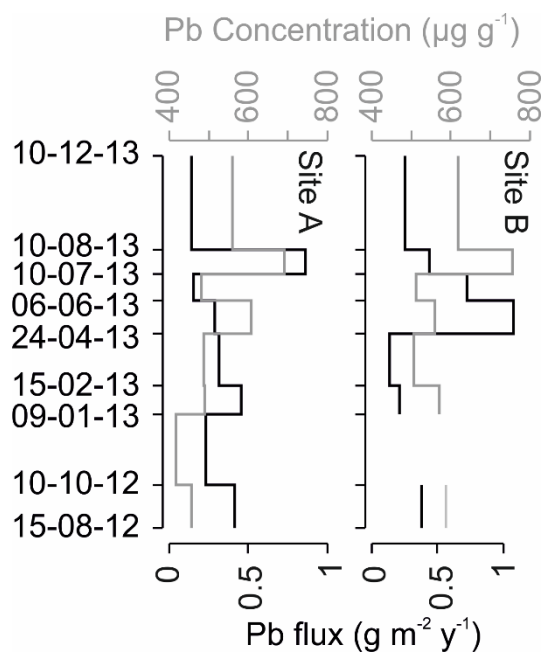


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